Can machines beat humans at electronic structure?

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http://dft.uci.edu

A. Review of DFT

The electronic structure problem

- Use atomic units
- Born-Oppenheimer approximation
- All non-relativistic (but added back in)
- Wavefunctions antisymmetric and normalized
- Only discuss ground-state electronic problem here, but many variations.

Hamiltonian for N electrons in the presence of external potential $v(\mathbf{r})$:

$$\hat{H} = \hat{T} + \hat{V}_{\rm ee} + \hat{V},$$

where the kinetic and elec-elec repulsion energies are

$$\hat{T} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2, \qquad \hat{V}_{\rm ee} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j\neq i}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|},$$

and difference between systems is N and the one-body potential

$$\hat{V} = \sum_{i=1}^{N} v(\mathbf{r}_i)$$

Often $v(\mathbf{r})$ is electron-nucleus attraction

$$v(\mathbf{r}) = -\sum_{\alpha}\frac{Z_\alpha}{|\mathbf{r} - \mathbf{R}_\alpha|}$$

where α runs over all nuclei, plus weak applied **E** and **B** fields.

$$\{\hat{T} + \hat{V}_{\rm ee} + \hat{V}\}\,\Psi = E\,\Psi, \qquad E = \min_{\Psi}\langle\Psi|\hat{T} + \hat{V}_{\rm ee} + \hat{V}|\Psi\rangle$$

DFT method

1964: HK theorem: There exists F[n]

Define *fictitious* non-interacting electrons satisfying:

$$\left\{-\frac{1}{2}\nabla^2 + v_{\rm S}(\mathbf{r})\right\}\phi_j(\mathbf{r}) = \epsilon_j\phi_j(\mathbf{r}), \qquad \sum_{j=1}^{N}|\phi_j(\mathbf{r})|^2 = n(\mathbf{r}).$$

where $v_{\rm S}(\mathbf{r})$ is *defined* to yield $n(\mathbf{r})$.

Define $T_{\rm S}$ as the kinetic energy of the KS electrons, U as their Hartree energy and

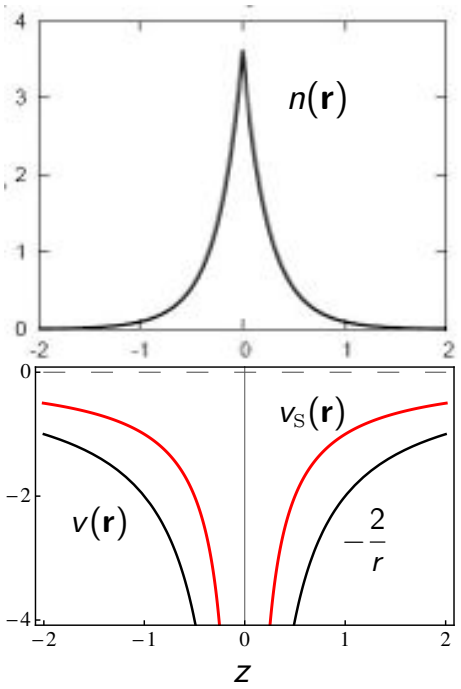
$$T + V_{\rm ee} = T_{\rm S} + U + E_{\rm XC}$$

the remainder is the exchange-correlation energy.

Most important result of exact DFT:

$$v_{\rm S}(\mathbf{r}) = v(\mathbf{r}) + \int d^3r \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + v_{\rm XC}[n](\mathbf{r}), \qquad v_{\rm XC}(\mathbf{r}) = \frac{\delta E_{\rm XC}}{\delta n(\mathbf{r})}$$

Knowing $E_{\rm XC}[n]$ gives closed set of self-consistent equations.



Orbital-free DFT: Approximate $T_s[n]$ directly, and go much, much faster.

Local approximations=semiclassical

- Consider scaling to continuum limit:

$$v^{\zeta}(\mathbf{r}) = \zeta^{1+1/d}\, v(\zeta^{1/d}\mathbf{r}) \,, \qquad N \to \zeta N.$$

  where d is spatial dimension.
- Lieb and Simon (1973) proved that Thomas-Fermi theory is relatively exact as $\zeta \to \infty$, i.e.,

$$\frac{E^{\mathrm{TF}} - E_0}{E_0} \to 0$$

- Equivalent to changing $Z = N$ for neutral atoms.
- Schwinger and Englert showed LDA exchange is relatively exact for atoms as $Z \to \infty$

Kieron's conjecture

Almost certain that

- $E_{\rm xc}^{\rm LDA}$ is relatively exact in the $\zeta \to \infty$ limit

$$\lim_{\zeta\to\infty} \frac{\Delta E_{\rm xc}^{\rm LDA}}{E_{\rm XC}} = \frac{E_{\rm xc}^{LDA} - E_{\rm xc}}{E_{\rm XC}} = 0$$

Kieron's instinct:

- Success of simple local-type approximations is because they are crude attempts to capture leading corrections to asymptotic limit (LDA)

Corollary: Leading corrections to LDA in this limit ARE what we are trying to capture with more accurate DFT approximations

Semiclassical work in progress

- Almost exact exchange at almost no cost
  - for 1d boxes, do LDA calculation, then evaluate semiclassical exchange.
- Semiclassical holes versus LDA/GGA holes
  - For 1d boxes, see huge improvement over LDA holes, pointwise in space
- Turning points
  - Finally derived and proved formulas in presence of turning points
- RPA correlation energy of atoms
  - Very bizarrely fits semiclassical limit


Attila Cangi


Hardy Gross


Raphael Ribeiro

B. Strong correlation

- Ongoing project with Steve White at UCI
- Apply DMRG to continuum problems


Thomas E. Baker


Lucas Wagner


Miles Stoudenmire


Steve White

Mott-Hubbard gap

- Classic prototype of condensed matter
- Infinite chain of H atoms
- When lattice spacing is large, must be an insulator
- But with one electron per site, always a band metal

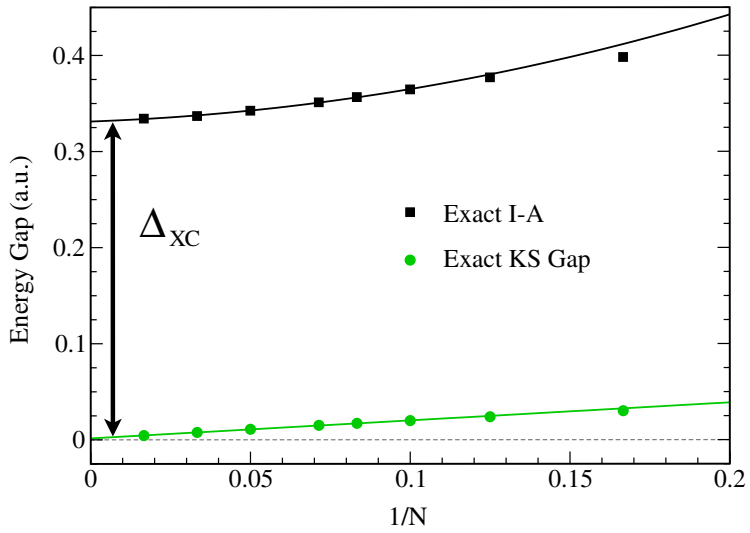


FIG. 3 (color online). Exact gaps for chains of N soft hydrogen atoms with atomic separation $b = 4$ (error bars are less than symbol sizes). The upper curve is a quadratic fit of exact gaps of the largest six systems and extrapolates to a finite value $E_g \simeq 0.33$. The exact Kohn-Sham gaps, in contrast, extrapolate to zero showing that for $N \to \infty$ the true KS system is metallic (lower curve is a linear fit of exat KS gaps of the largest six systems).

One-Dimensional Continuum Electronic Structure with the Density-Matrix Renormalization Group and Its Implications for Density-Functional Theory E.M. Stoudenmire, Lucas O. Wagner, Steven R. White, Kieron Burke, Phys. Rev. Lett. **109**, 056402 (2012).

Proof of convergence of KS eqns

- Lemma: $\int d^3 r (v[n'](\mathbf{r}) - v[n](\mathbf{r}))(n'(\mathbf{r}) - n(\mathbf{r})) < 0.$
- Oops: Already proven by Gritsenko and Baerends (2005) – see our erratum.
- Consequence: take one step for some
  - dE/dλ always < 0 at ends of curve
  - Guarantees a minimum
  - Can prove always converges for $\lambda < \lambda_c$
  - Assume Hilbert space finite

Guaranteed Convergence of the Kohn-Sham Equations Lucas O. Wagner, E. M. Stoudenmire, Kieron Burke, Steven R. White, Phys. Rev. Lett. **111**, 093003 (2013).

Kohn–Sham calculations with the exact functional Lucas O. Wagner, Thomas E. Baker, E. M. Stoudenmire, Kieron Burke, Steven R. White, Phys. Rev. B (submitted) (2014).

Semiclassical origins of strong correlation

- Consider $v_s(r)$ as function of bond length R
- For exact KS potential, new turning points occur at about R=3.3 Å
- Coulson-Fischer point (where spontaneous symmetry is broken) is 3.3 Å in LDA
- Beyond that point (i.e., for strongly correlated systems), there is a different asymptotic expansion!
- Explains failure of local approximations for strongly-correlated systems.

C. Machines

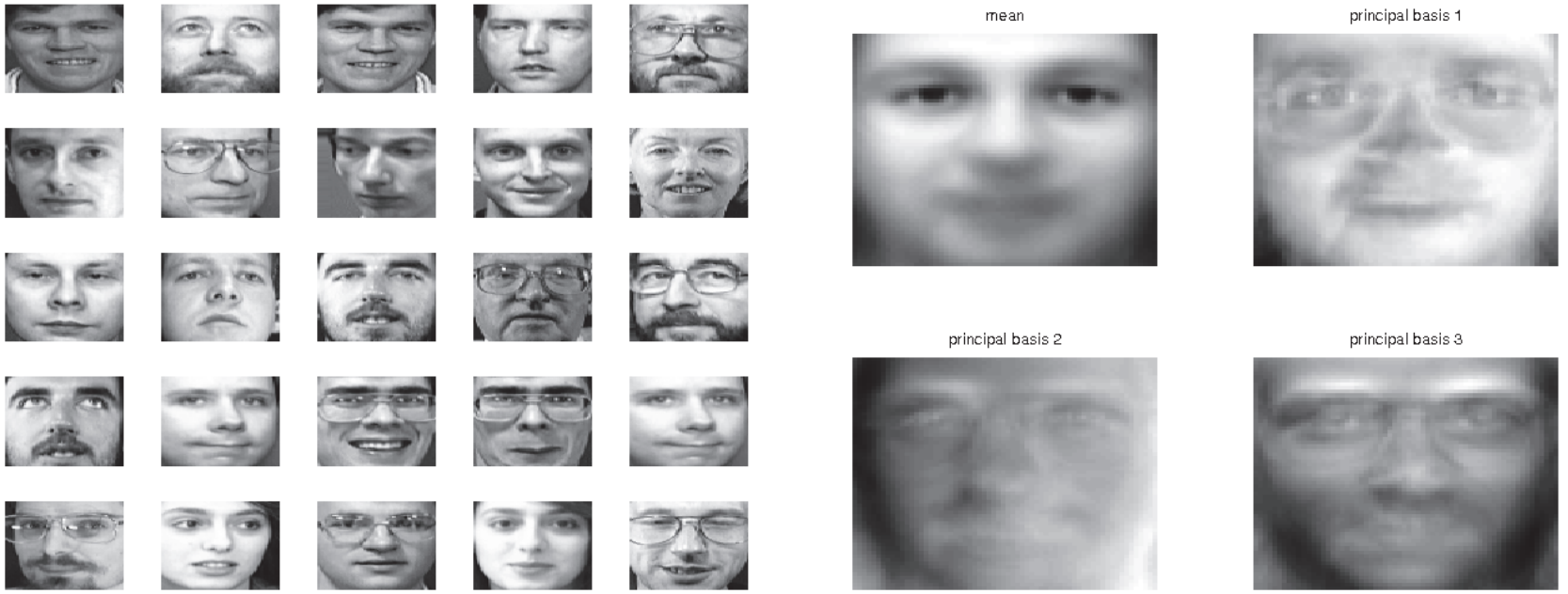


Figure 1.10 a) 25 randomly chosen 64×64 pixel images from the Olivetti face database. (b) The mean and the first three principal component basis vectors (eigenfaces). Figure generated by `pcaImageDemo`.

Machine learning

- Powerful branch of artificial intelligence
- Essentially fitting and interpolating
- Maps problem into much higher-dimension feature space, using a simple kernel
- Higher-dimension often means more linear
- Perform regression in feature space
- Project back to original problem

Kernel ridge regression

- Kernel ridge regression (KRR). Given $\{\mathbf{x}_j, f_j\}$

$$\hat{f}(\mathbf{x}) = \sum_{j=1}^{M} \alpha_j k(\mathbf{x}_j, \mathbf{x})$$

$$k(\mathbf{x}, \mathbf{x}') = \exp(-\|\mathbf{x} - \mathbf{x}'\|^2/(2\sigma^2))$$

length scale

- Minimize:

$$\mathcal{C}(\boldsymbol{\alpha}) = \sum_{j=1}^{M} (\hat{f}(\mathbf{x}_j) - f_j)^2 + \lambda^2 \|\alpha\|^2$$

noise level

$$\boldsymbol{\alpha} = (K + \lambda^2 I)^{-1} \mathbf{f}$$

ML applications in electronic structure

- All driven by Klaus Mueller of TU Berlin, computer science.


Klaus-Robert Müller

- ML now being applied directly to, e.g., molecular energies from geometries for drug design, many by Matthias Rupp (U. Basel)


Matthias Rupp

- Our efforts are focussed on finding $T_s[n]$ from examples, headed by John Snyder (Humboldt fellow at TU Berlin/MPI Halle)


John Snyder

Demo problem in DFT

- *N* non-interacting same-spin fermions confined to 1d box
- Define class of potential:

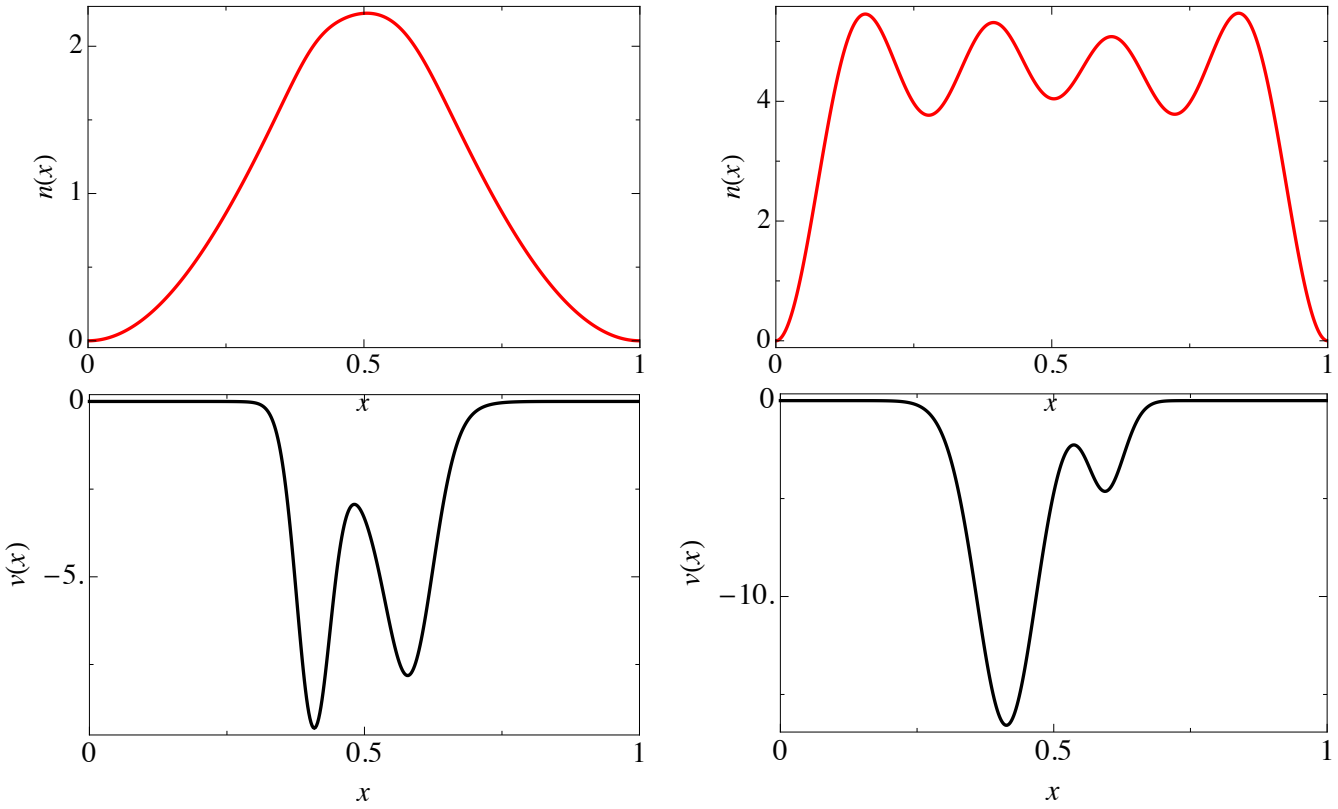
$$v(x) = -\sum_{i=1}^{3} a_i \exp(-(x-b_i)^2/(2c_i^2))$$

- Represent the density on a grid with spacing $\Delta x = 1/(G-1)$
- ML-DFA for KE:

$$\hat{T}(\mathbf{n}) = \bar{T} \sum_{j=1}^{M} \alpha_j k(\mathbf{n}_j, \mathbf{n})$$

Dataset

Generate 2000 potentials. Solve for up to 4 electrons.



Performance for T_s

kcal/mol

N	M	λ	σ	$\overline{\lvert\Delta T\rvert}$	$\lvert\Delta T\rvert^{\mathrm{std}}$	$\lvert\Delta T\rvert^{\mathrm{max}}$
1	40	2.4×10^{-5}	238	3.3	3.0	23.
	60	1.0×10^{-5}	95	1.2	1.2	10.
	80	6.7×10^{-6}	48	0.43	0.54	7.1
	100	3.4×10^{-7}	43	0.15	0.24	3.2
	150	2.5×10^{-7}	33	0.060	0.10	1.3
	200	1.7×10^{-7}	28	0.031	0.053	0.65
2	100	1.3×10^{-7}	52	0.13	0.20	1.8
3	100	2.0×10^{-7}	74	0.12	0.18	1.8
4	100	1.4×10^{-7}	73	0.078	0.14	2.3
1-4†	400	1.8×10^{-7}	47	0.12	0.20	3.6

LDA ~ 223 kcal/mol, Gradient correction ~ 159 kcal/mol

functional derivative?

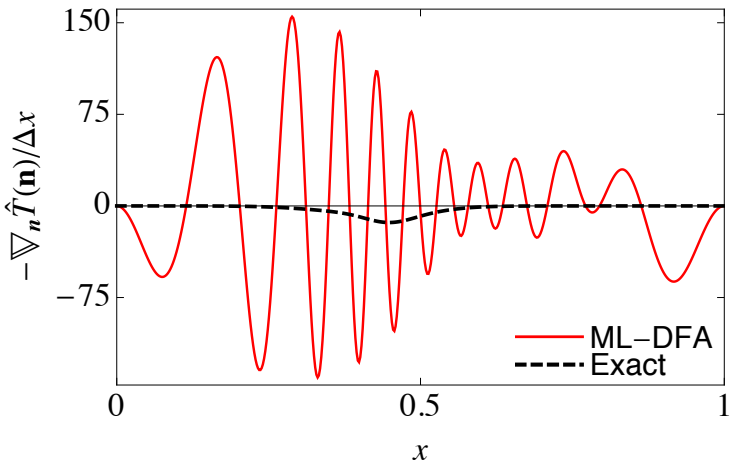
Exact

$$\frac{\delta T[n]}{\delta n(x)} = \mu - v(x)$$

ML-DFA

$$\frac{1}{\Delta x}\nabla_{\mathbf{n}}\hat{T}(\mathbf{n}) = \sum_{j=1}^{M} \alpha'_j(\mathbf{n}_j - \mathbf{n})k(\mathbf{n}_j, \mathbf{n})$$

$$\alpha'_j = \alpha_j/(\sigma^2\Delta x)$$



- Functionals are defined on infinite-dimensional spaces
- With finite interpolation, can always find bad directions
- Can we make a cruder definition that will work for our purposes?

Principal component analysis

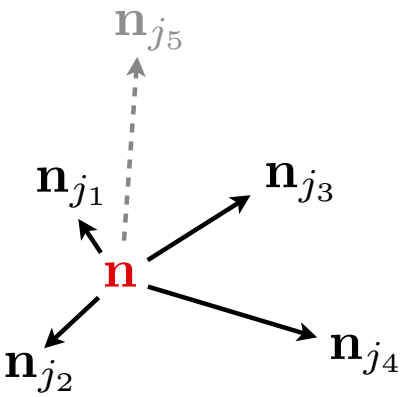
$$X = (\mathbf{n}_{j_1} - \mathbf{n}, \ldots, \mathbf{n}_{j_m} - \mathbf{n})^\top$$

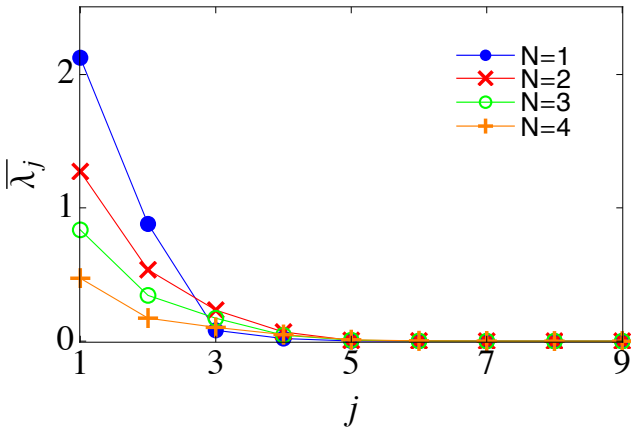
$$C = \frac{1}{m} X^\top X$$

$$\lambda_j, \mathbf{x}_j$$

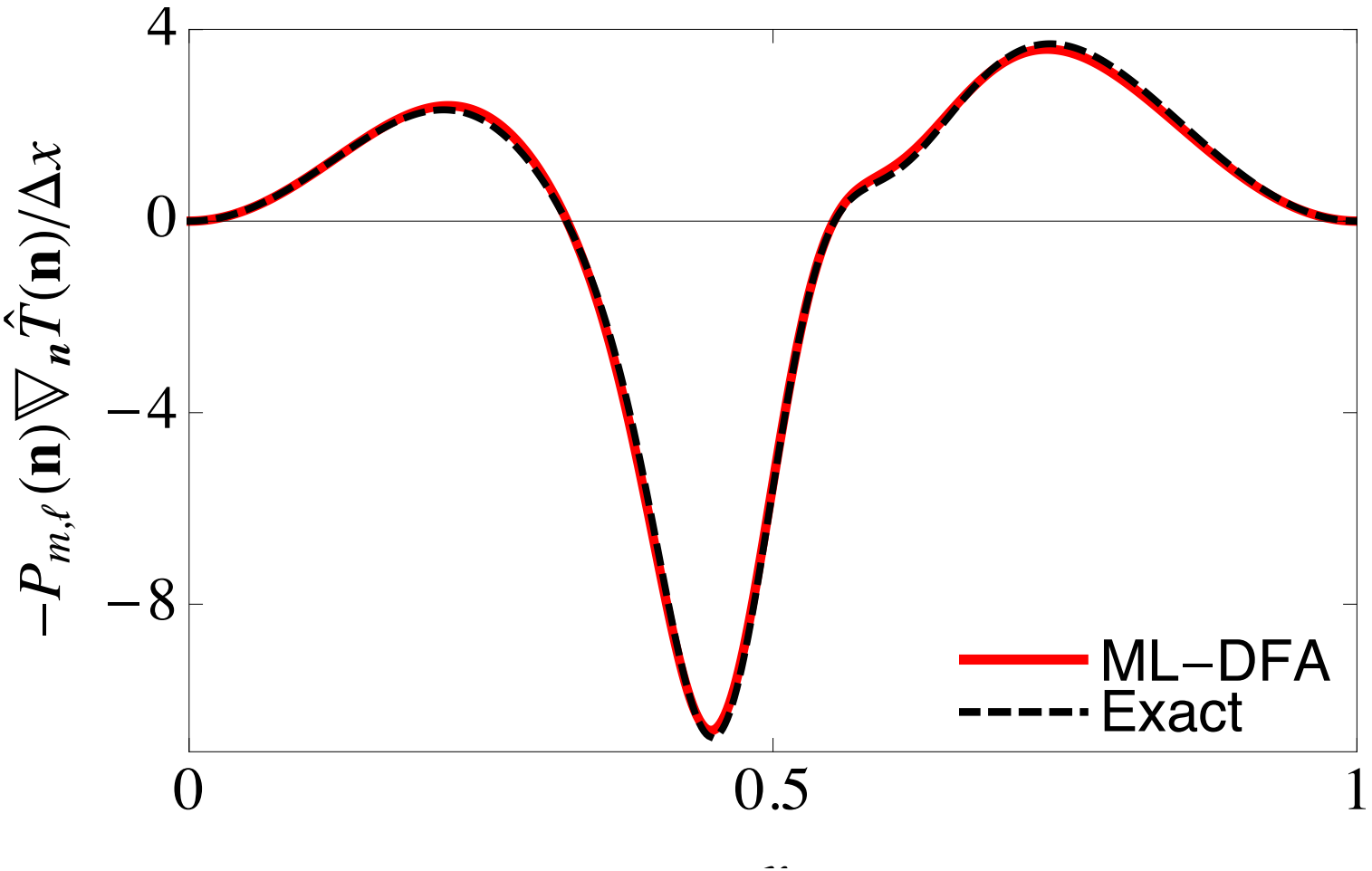
$$P_{m,\ell}(\mathbf{n}) = V^\top V$$

$$V = (\mathbf{x}_1, \ldots, \mathbf{x}_\ell)^\top$$





Projected functional derivative

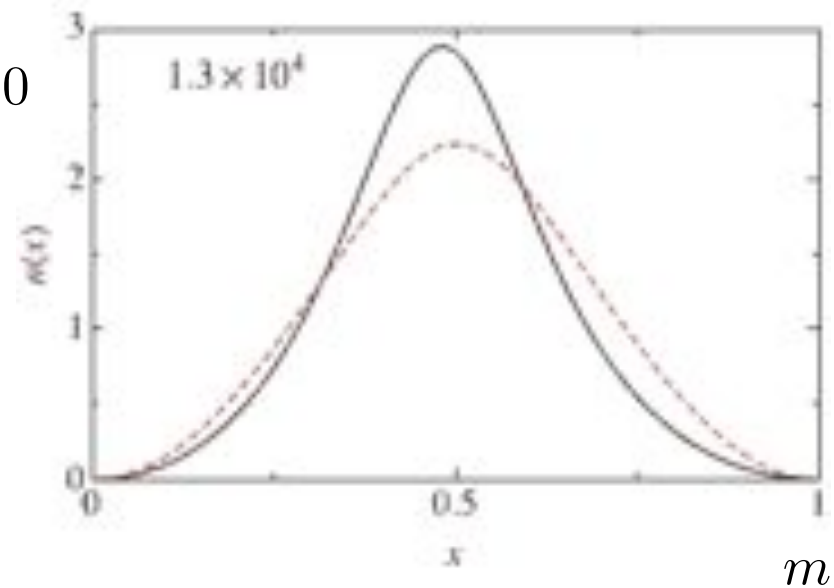


Constrained optimized density

- Gradient descent search:

$$\mathbf{n}^{(j+1)} = \mathbf{n}^{(j)} - \epsilon P_{m,\ell}(\mathbf{n}^{(j)})(\mathbf{v} + \nabla_{\mathbf{n}} \hat{T}(\mathbf{n}^{(j)})/\Delta x)$$

$N = 1$
$M = 100$

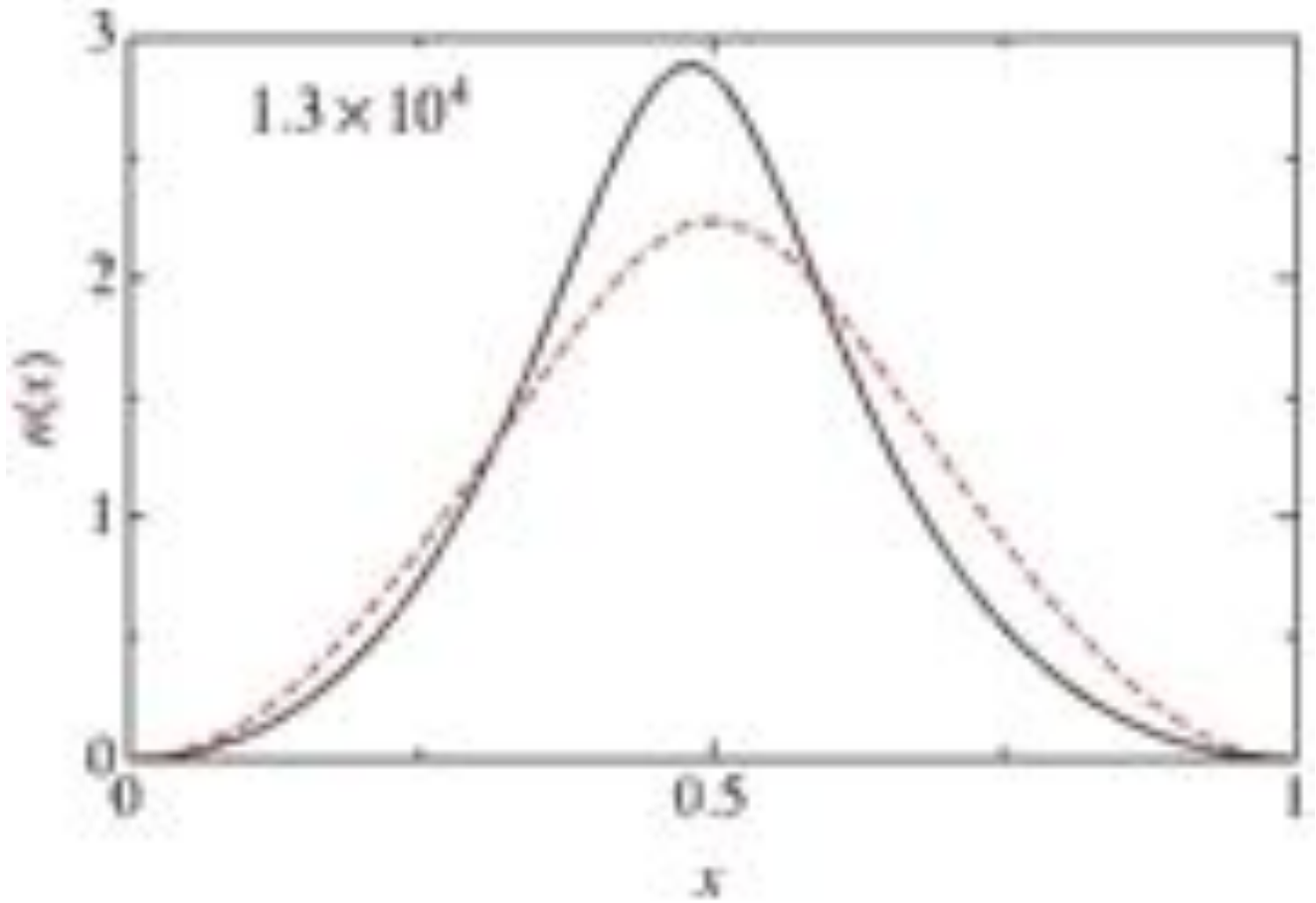


$\Delta T_j = 0.154$ kcal/mol
$\Delta T_j^{\text{sc}} = 6.53$ kcal/mol

Ratio $= 43$

$m = 15, \ell = 5$

SC density movie



First ‘ML meets DFT’ paper

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28	1.94645582566549	2.751346713386582	0.0948195528516815	0.4901204212506473	7.863592227266858	0.0951797983951825	0.5196620049802691	9.51608680035275	0.07785377315463609	0.5806015592262945
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30	−3.886381532577754	4.95871172966177	0.06823254438777603	0.5645951313008806	9.08135225317634	0.04472856905840844	0.4299117124064201	8.24973637849809	0.08854431361856	0.5416193648861009
31	−1.341930696378109	6.451869235304859	0.05482804889270922	0.5694170176403242	4.416924333519995	0.04212208612720639	0.5897125000677342	8.86521100790565	0.0866581794842557	0.5311744230227635
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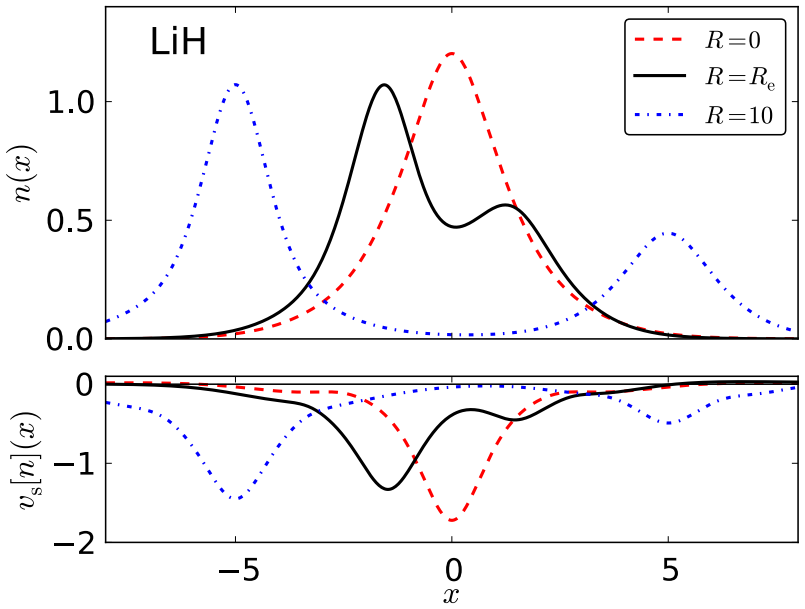
58	3.395104400983763	7.973680986292	0.0911843583955236	0.5314007871406556	6.375772536276909	0.0933026364108379	0.447244215655568	7.387561983870292	0.0977643384454912	0.479824590293356
59	1.330224789015745	5.105339790874075	0.06331718284342962	0.5503804706506275	9.5740821641842	0.07463500644132846	0.5814481952546582	5.810342341443878	0.03327635127803191	0.5550216356360829
60	−0.2920604955263079	6.773414983805557	0.07595819905259191	0.5210834626114553	4.229974804881476	0.03532177545633547	0.5725615130215063	8.88452823254966	0.0932985710685446	0.5046388124857028
61	−26.41840990525562	6.41701161854283	0.06246944646172664	0.4258923441426071	1.379491105318868	0.06306367927818108	0.4531443030507202	2.189456974183496	0.098078005933584	0.5174384564079299
62	6.630393088825135	6.476325542442256	0.07599435647188182	0.4345528705798566	6.969363897694016	0.0666930203716108	0.517427894398595	3.961825639220393	0.0929115322244988	0.4621045370336795
63	3.065748817227897	1.300093759156537	0.06741885075599173	0.4866345116967513	6.942052331590217	0.07107963920756023	0.4930672781311588	7.834870626014938	0.06446115603870624	0.5367219218216266
64	−1.743105697039855	3.145607697855832	0.0415292						0.07636214080338054	0.4330291254331895
65	−1.631255302904965	3.121291975208031	0.0313356						0.0936192481138518	0.4523240987335903
66	−9.50982692642515	7.367027947839741	0.0739810						0.04986976063479617	0.5394709698394433
67	−4.496736421068983	8.56498650586069	0.0870950						0.05651923264880363	0.4832351547748815
68	−1.002977917543076	9.43121814362608	0.0368989						0.05983735955021298	0.48375600350014 34
69	−9.23106545170694	8.4792969615945 9	0.0547214						0.06892772167363432	0.5908529311844791
70	14.99926304831282	4.708917711658332	0.0907364						0.05825558914206748	0.566434199642786
71	4.189181104505013	7.583635162152007	0.0936829						0.04763840334231468	0.5010633160850224
72	8.32837188138842	3.414315967033806	0.05054048464274665	0.5043307410524706	3.070996567281799	0.06968276328974509	0.5702669702356848	5.360783854112533	0.0388888383066967	0.5784155467566237
73	−21.84200888491582	1.625552430388586	0.04546236831654488	0.5426078576324179	4.091176923293506	0.03836885039652842	0.504879512949007	4.527748284314512	0.05975894102927981	0.4670598506496871
74	6.604738977945651	3.42187897931262	0.0894449950697187	0.4941485628974172	4.96749741331263	0.06031151123783582	0.4119028637456998	4.581927607849956	0.0871948963692279	0.4176805754532423
75	15.27988423246628	6.229538426957454	0.0821521091215863	0.4118748449252315	2.377028497509498	0.0963110933106458	0.4746736556808109	5.398545541594487	0.0822574656780643	0.5258947233190487

Finding Density Functionals with Machine Learning John C. Snyder, Matthias Rupp, Katja Hansen, Klaus-Robert Müller, Kieron Burke, Phys. Rev. Lett. **108**, 253002 (2012)

Bond-breaking with ML

- Performed many 1d KS calculations of diatomics as function of bond length, using LDA with soft-Coulomb repulsion, including several with more than 2 electrons



Orbital-free Bond Breaking via Machine Learning John C. Snyder, Matthias Rupp, Katja Hansen, Leo Blooston, Klaus-Robert Müller, Kieron Burke, J. Chem. Phys. **139**, 224104 (2013)

Constrained optimal density

- Convergence of constrained optimal density with # of training points.

Kernels, Pre-Images and Optimization John Snyder, Sebastian Mika, Kieron Burke, Klaus-Robert Müller, Chapter in Empirical Inference - Festschrift in Honor of Vladimir N. Vapnik (2013)

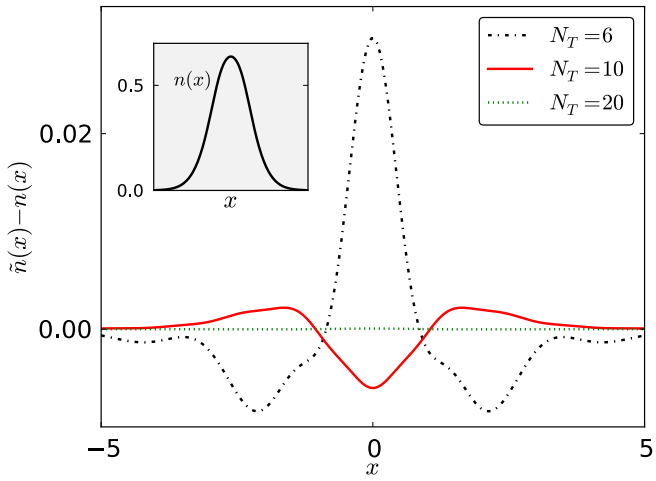


FIG. 7. Difference between the constrained optimal density $\tilde{n}(x)$ and the KS density $n(x)$ for various numbers of training densities N_T. The error decreases uniformly for all x. The system is H_2 at equilibrium bond length. The inset shows the KS density.

Types of errors in DFT

- $\Delta E_F = \bar{E}_{xc}[n]-E_{xc}[n]$
- $\Delta E_D = \bar{E}_{xc}[\tilde{n}]-\bar{E}_{xc}[n]$
- $\Delta E = \Delta E_F + \Delta E_D$
- Error analysis of energies in kcal/mol as a function of R with different numbers of training data, on constrained optimal densities

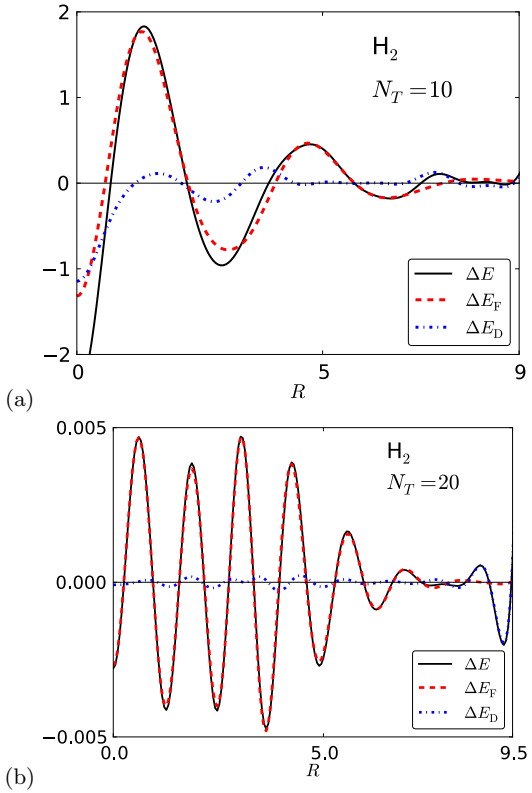


FIG. 8. The total error of the model and the functional- and density-driven errors ΔE_F and ΔE_D for H_2 with (a) 10 and (b) 20 training densities.

Functional derivatives and densities

- How can we get accurate densities from lousy derivatives?
- Once solution density is within interpolation manifold, simply constrain derivative to stay on that manifold
- Analogy:
  - Problem: find global minimum of 2D surface, given exact data along a 1D curve in that surface that passes through the minimum.
  - Solution: Make sure you stay on the path.
- PS: Inspired density-corrected DFT, which corrects many self-interaction errors!

Understanding and reducing errors in density functional calculations Min-Cheol Kim, Eunji Sim, Kieron Burke, Phys. Rev. Lett. **111**, 073003 (2013).

Ions in solution: Density corrected density functional theory (DC-DFT) Min-Cheol Kim, Eunji Sim, Kieron Burke, The Journal of Chemical Physics **140**, 18A528 (2014)


Eunji Sim

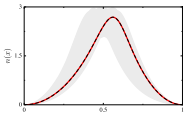

Min-Cheol Kim

Conceptual relationship

- ML works when
  a) There's a rule
  b) Rule is too complicated for humans
  c) There's data
- HK theorems say
  a) There is a functional
  b) It cannot be given explicitly, exactly
  c) Examples give exact values
- More important, practically:
  – In chemistry and materials, we only care about solutions to an absurdly small fraction of possible problems, i.e., nuclear potentials at various positions, so underlying dimensionality of solutions is very small, just solving differential equation is hard.

Road map back to reality

Roadmap to 3d land

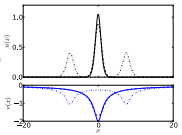


1d box

model selection, projected functional derivatives, OF-DFT

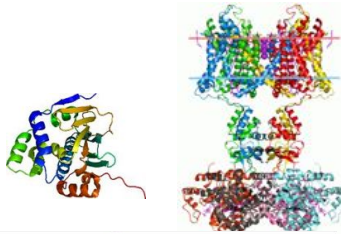
bond breaking, self-consistent densities

1d diatomics

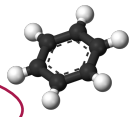


dimensionality, basis sets, representation, inversion symmetry

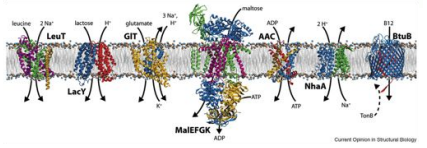
3d atoms, diatomics



full symmetries, scaling



3d molecules



scalability, data accumulation
ab-initio MD, active learning

large systems, real applications

D. Cross-fertilization

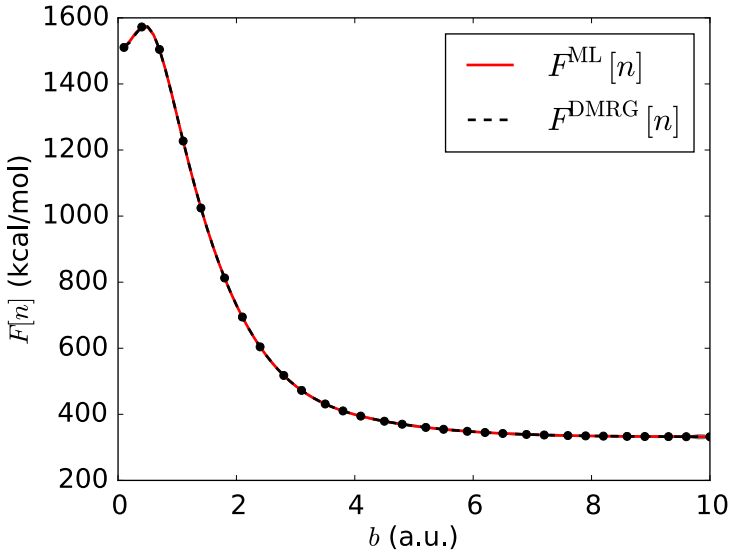
- All preliminary results (over weekend)

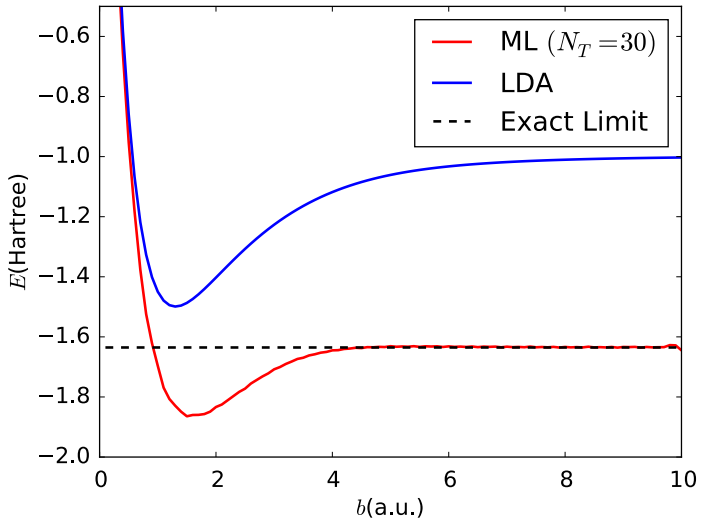
Li Li

Thomas E. Baker

DMRG meets DFT meets ML

- Ran H_4 with fixed separations b using DMRG (exp repulsion)
- Use 30 values of b to train ML version of exact F[n]
- Yields accurate exact binding energy curve self-consistently.





Summary

- ML of functionals works to produce highly accurate approximate functionals
- Totally different approach from anything before
- ML can even
  - find accurate densities
  - say when it will work within tolerance
  - break bonds
  - Do the full functional
- But
  - only demonstrated in 1d
  - Need to do arbitrary-sized system
- Thanks to
  - Students: Li Li, John Snyder, Kevin Vu, Isabelle Pelaschier
  - Collaborators: Klaus Mueller, Matthias Rupp, Katia Hansen
  - Funders: NSF from chem, DMR, math